The Effect of Air Oxidation on the Caking Properties of Pittsburgh-Seam Coal

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INTRODUCTION

Production of synthetic liquid and gas fuels is a potential means for increasing the market for coal. The demand for fuel is high in the East and Midwest, but unfortunately most coals in these sections become sticky and agglomerate or cake when they are heated through the range of 300°-400° C. If they could be made noncaking, they would be suitable for fluidized-bed gasification, hydrogenation, and carbonization.

Nathan[7/] destroyed the caking property of coal (10 to 400 mesh) by pretreating it in air at 316°-441° C. Channabasappa[1/] treated coal of 88 to 98 percent through 100 mesh with air as well as other gases at a temperature range of 200°-382° C. Schmidt[8/] decaked Pittsburgh-seam coal of 0 to 1/4-inch size with air at 99.3° C. He also noted that the agglutinating value of the coals decreased as the oxidation of the coals increased. Minet[6/] oxidized coal with steam plus air at 370°-430° C in the first stage of a carbonization process, and Williams[9/] treated coal (80 percent through 1/8 inch screen) with an oxygen-containing gas at 80°-300° C.

Pittsburgh-seam coal is highly caking. In earlier work at the Bureau[2/] it was made nonagglomerating, and with only slight variation the treatment was successfully applied to other caking coals. In this previous work the caking property of Pittsburgh-seam coal was destroyed by treating it in both static[4/] and fluidized[2,3/] beds with steam plus oxygen or air. To extend this study the present program was to treat Pittsburgh-seam coal with air only, to study the effect of operating variables such as mesh size, temperature, residence time and pressure, and to deduce the changes that may take place in the coal during treatment by carbonizing the treated coal.

Decaking was considered successful if the free-swelling index (FSI) of the treated coal (char) did not exceed 1-1/2 and the treated coal did not agglomerate when it was heated in a hydrogen atmosphere to 900° C.

STATIC-BED EXPERIMENTATION AND RESULTS

In the static-bed experiments fine particles of Pittsburgh-seam coal were spread in 100 x 50 ml dishes to a 1/2-inch depth, placed in a large drying oven, and heated in air to 95°-100° C. To decake these coals, using an FSI of 1-1/2 or less as indicating satisfactory decaking, required about 16 hours treatment under these conditions for 150-200 mesh[a/] coal, 24 hours for 100-150 mesh, and 50 hours for 48-100 mesh (figure 1). At the end of 64 hours the 18-48 mesh coal had an FSI of 3-1/2. The oxygen content of all coals increased with time; with the finer coals the increase was more rapid. The loss in volatile matter averaged about 3 percentage points (a change from 40 percent volatile matter in the raw to 37 percent in the treated coal). About 6 months after the original data were collected, additional tests were made on different batches of coal of 18-48 and 48-100 mesh sizes. These results are shown on figure 1 as larger squares and dots. While the later data with the 18-48 mesh coals correlate with the earlier results, data from the 48-100 mesh size show some discrepancies. These results, although not exact due to the method of operation, demonstrate that treating fine coal in air at 100° C will decake the coal, but at least 16 hours time will be needed. These tests also indicate that it is not safe to assume that there is no change in the properties of fine coal dried in air at this temperature.

FLUIDIZED-BED EXPERIMENTATION AND RESULTS

Apparatus for the fluid-bed experiments is shown in figure 2. The reactor is a stainless steel tube of 1-inch diameter with an expanded section of 2-inch diameter at the top. The 29-inch section containing the fluidized bed of coal is heated electrically. Thermocouples are inserted inside a well placed down through the center of the reactor. Raw coal from the continuous feeder is entrained in the air stream and carried into the bottom of the reactor. The oxygen in the air renders the coal noncaking at specified temperatures, and the treated coal overflows into a collection vessel. Gases, tars, and dusts are discharged from the top of the reactor.

Because the height of the fluidized bed is constant, the rate that the coal is fed determines the residence time of the coal in the reactor. Only 40 minutes were required to decake Pittsburgh-seam coal in the fluid bed at 200° C for the 150-200 mesh size and 400° C for the 18-48 and 48-100 mesh size (figure 3). The results are more relative than absolute, but the trends are realistic. The oxygen content of the coals reached a maximum between 300° and 400° C and was less at the higher temperatures. The

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a/ All mesh sizes are Tyler Standard Screen Series.

temperature at which it reached a maximum depended on the mesh size. As the temperature was raised to 300° C, the volatile-matter content decreased gradually, and then precipitously at higher temperatures. The minimum loss in volatile matter was about 3 percentage points at 300° C.

With the same 40-minute residence time the 150-200 mesh coal was treated at pressures of 1, 2, 5, and 10 atmospheres and 100° to 450° C (figure 4). At atmospheric pressure the coal became noncaking at 200° C; at 5 atmospheres it became noncaking at about 175° C, and at 10 atmospheres the coal burned above 150° C. At 150° C there was little change in the FSI. The oxygen content increased at higher pressures, the maximum being about 13 percent at 2 atmospheres and 300° C.

The volatile matter decreased at higher temperatures, but the change in volatile matter was insignificant at higher pressures. The least volatile matter was removed (3 percentage points) when the coal was treated at 200° C and atmospheric pressure.

Shortening the residence time to 20 minutes had little effect on the volatile matter and the FSI of the treated coal (figure 5) when compared with 40 minutes (figure 4). The amount of oxygen absorbed was the same as in the previous test at 2 atmospheres and 300° C. As the same results were obtained with the shorter residence times, the controlling variable seems to be temperature. Residence time might be shortened even more, but the limit of operability had been reached and the coal feed could not be increased to make such a test.

Also at the 20-minute residence time it was possible to continue the treatment at 5 atmospheres to 400° C, whereas at the 40-minute residence time the coal burned uncontrollably above 200° C. Thus the maximum oxygen content of the coal became 17 percent. Why coal could be treated at higher temperature with shorter residence time is not clear.

These curves show that the FSI is substantially independent of pressure, but highly dependent on coal size. More oxygen is absorbed by the coal at higher pressures and no more volatile matter is lost. The decrease in volatile matter is primarily a function of temperature, at least in the pressure range up to 10 atmospheres. Of course, when the pressure is increased, the air flow must also be increased to maintain fluidization; however, the oxygen/coal ratio at the different pressures indicates that pressure has more effect than air flow.

When the tests were made at 5 atmospheres, two samples of treated coal were taken at each temperature. One sample was evacuated to 30 mm absolute pressure to determine if oxygen taken up during treatment could be removed. Comparison with the nonevacuated sample showed that it could not. Consequently the additional oxygen must have chemically reacted in the coal to form a coal-oxygen complex.

CARBONIZATION TESTS: EXPERIMENTATION AND RESULTS

Comparing the results of low-temperature carbonization of coal fluidized in air at 230° C with raw coal gives a clue as to what changes take place in the volatile matter during the air treatment (table 1). The carbonization unit has a charging vessel at the top (figure 6)[2]. After the reactor reached the desired temperature, the valve below the charging vessel was opened to allow the coal to drop into the heated zone.

TABLE 1.- Batch carbonization tests at 538° C (1,000° F) and 427° C (800° F) at 30-minute residence time

Type of coal	Raw	Treated[1]	
Temperature, °C	538	538	427
Gas analysis, vol-pct			
H_2	13	10	2
N_2	0	0	1
CO	6	16	19
CH_4	53	39	17
C_2+	22	13	9
CO_2	6	22	52
HV	1060	750	410
Cubic feet tail gas per ton feed coal	1100	1600	400
Solids feed analysis, wt-pct, MAF			
Volatile matter	40.2	35.6	36.4
Fixed carbon	59.8	64.4	63.6
Hydrogen	5.6	4.8	4.9
Carbon	83.6	80.1	80.3
Nitrogen	2.3	2.2	1.6
Oxygen	6.6	11.1	11.2
Sulfur	1.9	1.8	2.0

1/ Made by fluidizing coal in air at 230° C for 30 minutes.

Proximate analysis (table 1) shows that treated and raw coals differ mainly in their volatile matter and oxygen content, the treated coal containing the more oxygen. The higher the oxygen content in the feed, the more carbon oxides in the gas produced by carbonization at 538°--12 percent for raw and 38 percent for treated coal. The heating value of the gas decreased as the carbon oxide yield increased, dropping from 1,060 to 750 Btu per cubic foot. This observation on carbon oxides is in agreement with the data of Juntgen[5] and of Schmidt[8].

The quality of the volatile matter differs for raw and treated coal. The treated coal carbonized at 427° C yielded primarily carbon oxides (table 1), indicating that the additional oxygenated compounds in the treated coals are reacted faster than the volatile matter in the raw coal. At 538° C the percentage of carbon oxides is less because after the supply of oxygenated compounds is depleted, the usual pyrolitic reactions predominate.

Table 1 gives the volatile matter of the raw coal as 40.2 percent and that of the treated coal as 35.6 percent. The larger quantities of carbon oxides given off during carbonization of the treated coal indicate that its volatile matter has been supplemented by the oxygenated compounds formed during treatment.

CONCLUSION

Tests show that Pittsburgh-seam coal, a highly caking coal, can be made nonagglomerating by heating in air in a static bed at 100° C for about 16 hours (150-200 mesh) or 50 hours (48-100 mesh).

In a fluid-bed reactor the finer mesh coal (150-200 mesh) can be made noncaking in 40 minutes by treating and fluidizing it with air at 200° C. As the temperature is increased, more oxygen combines with the coal until at about 350° C (depending on the coal size) the burning of the coal becomes uncontrollable. The percentage of oxygen in the coal increased from about 8 percent in the raw coal to as high as 17 percent when the coal was treated at 5 atmospheres pressure. Satisfactory decaking (as indicated by an FSI of 1-1/2 or less) was obtained with a volatile loss of 3 percentage points (10 percent of the volatile matter).

Carbonization tests indicate by the greatly increased yield of carbon oxides from the treated over the raw coal that a large amount of oxygenated compounds is included in the volatile matter of the treated coal. These additional compounds had to come from the treatment.

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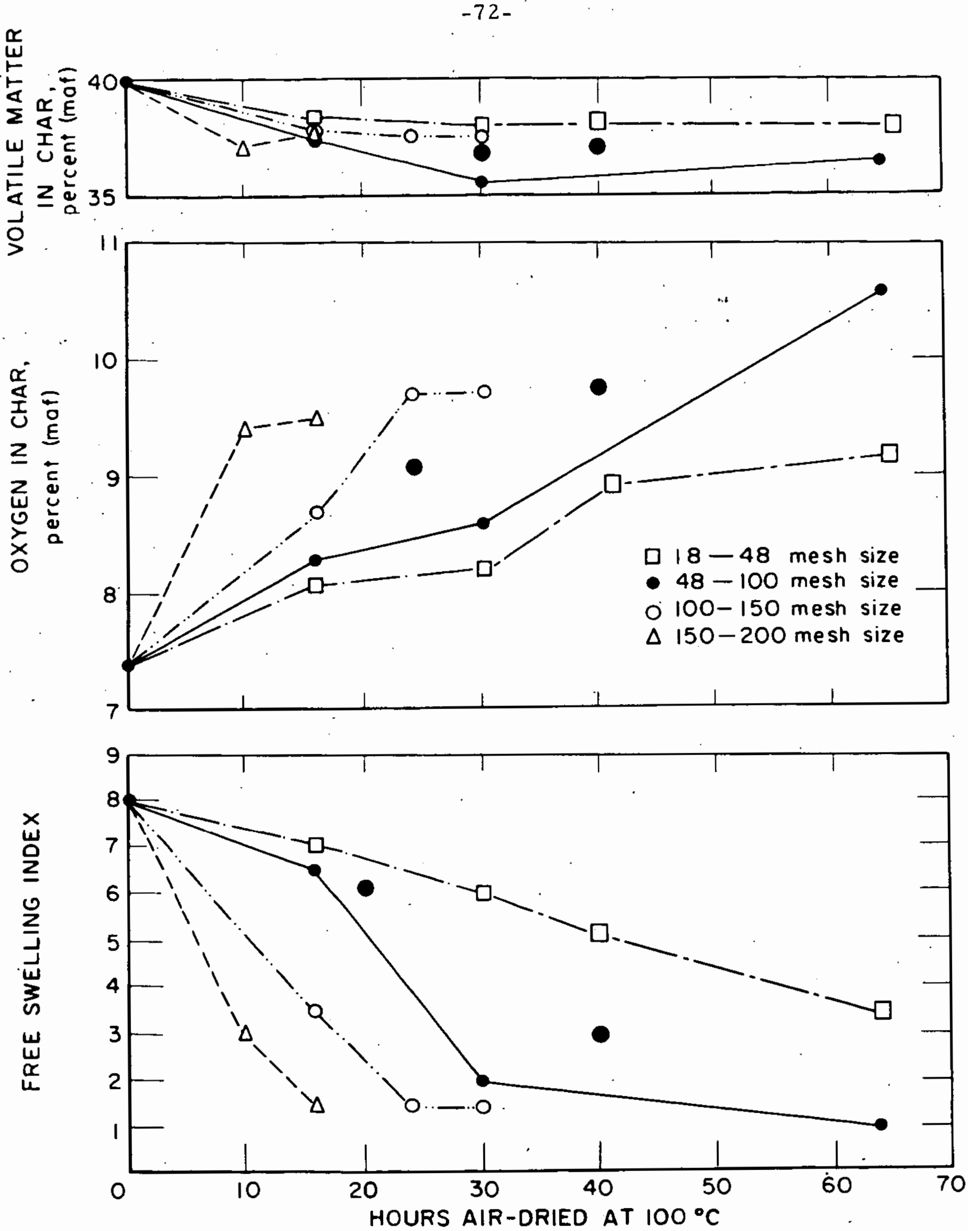

Fig. 1.-EFFECT OF RESIDENCE TIME ON THE FSI, VOLATILE MATTER, AND OXYGEN CONTENT OF CHAR OF PITTSBURGH-SEAM COAL TREATED IN AIR AT 100°C IN A STATIC BED

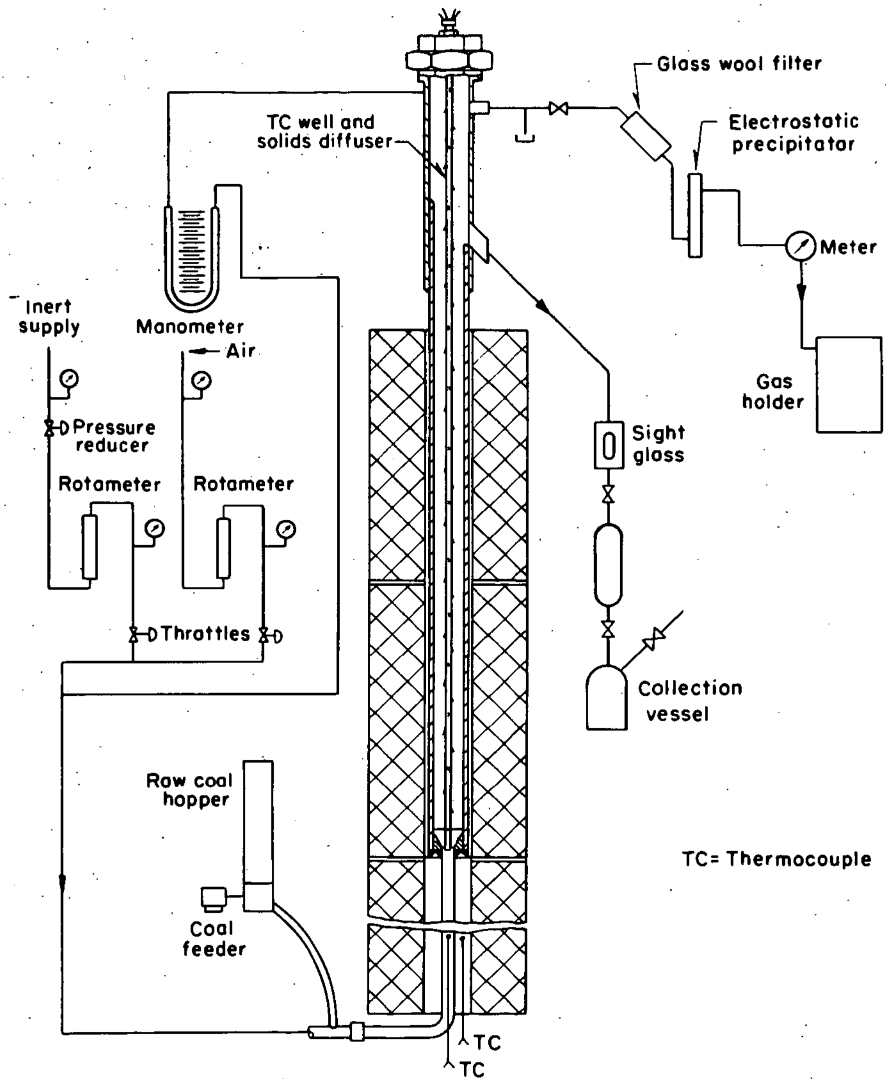

Fig. 2.-CONTINUOUS FLUIDIZED-BED COAL PRETREATER

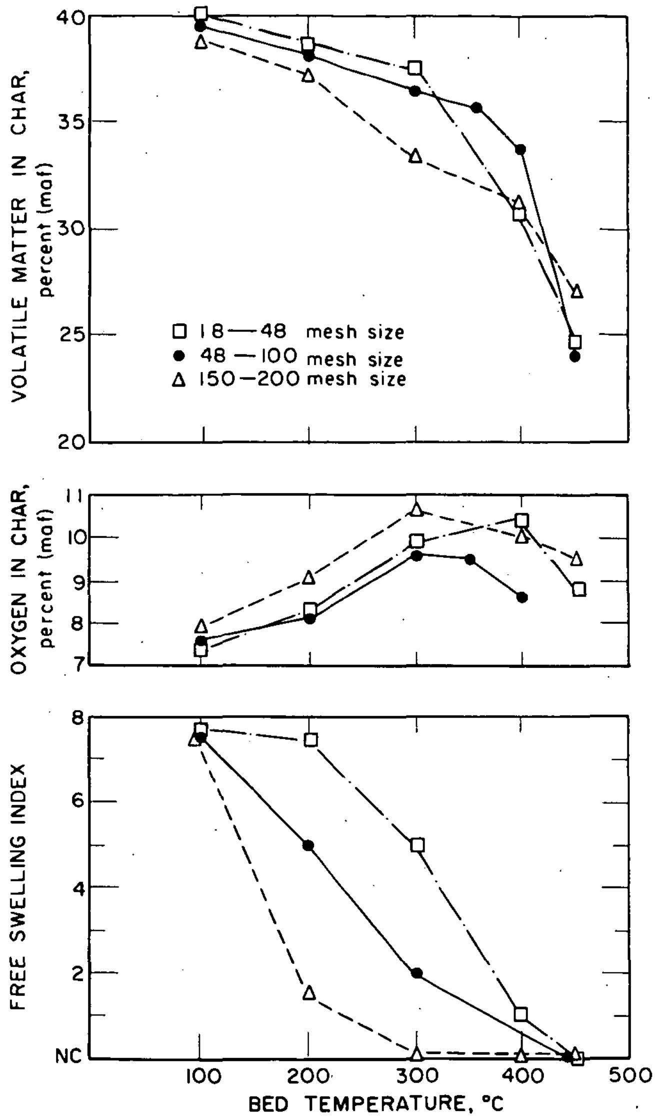

Fig. 3.-EFFECT OF TEMPERATURE DURING AIR TREATMENT IN A FLUID BED ON THE FSI, VOLATILE MATTER, AND OXYGEN CONTENT OF CHARS OF PITTSBURGH-SEAM COAL. RESIDENCE TIME IS ABOUT 40 MINUTES.

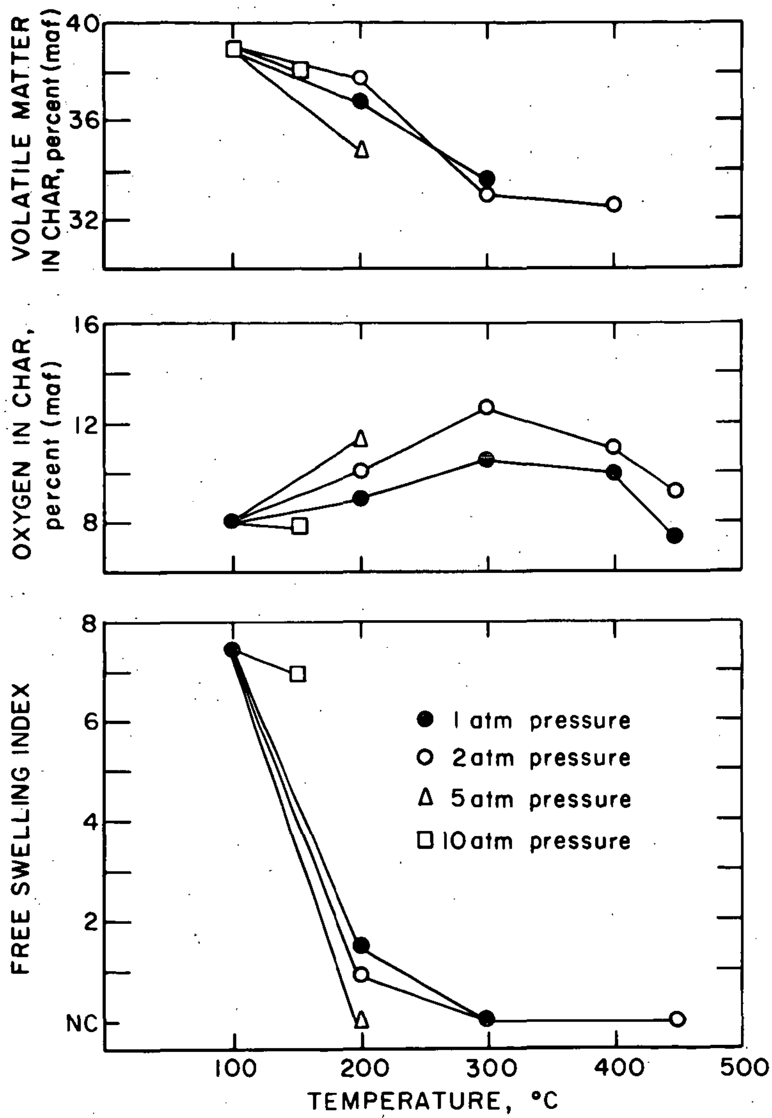

Fig. 4.-EFFECT OF PRESSURE DURING AIR OXIDATION IN A FLUID BED OF PITTSBURGH-SEAM COAL (150-200 MESH) ON FSI, VOLATILE MATTER, AND OXYGEN CONTENT OF CHAR. RESIDENCE TIME IS 40 MINUTES.

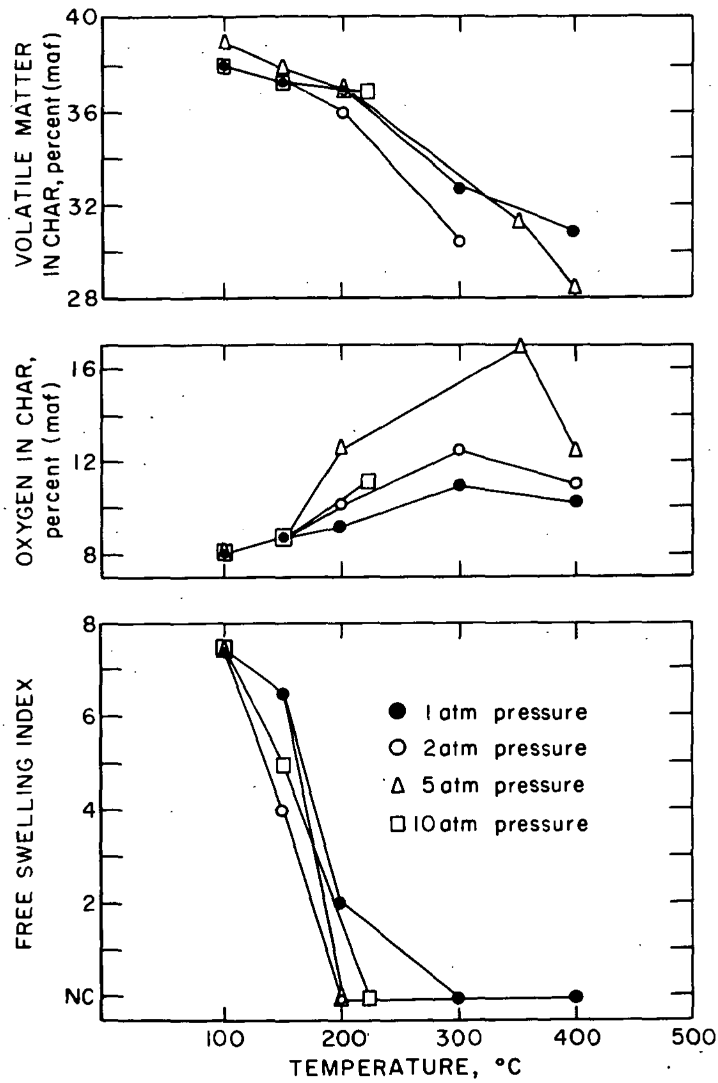

Fig. 5.-EFFECT OF PRESSURE DURING AIR OXIDATION IN A FLUID BED OF PITTSBURGH-SEAM COAL (150-200 MESH) ON FSI, VOLATILE MATTER, AND OXYGEN CONTENT OF CHAR. RESIDENCE TIME IS 20 MINUTES.

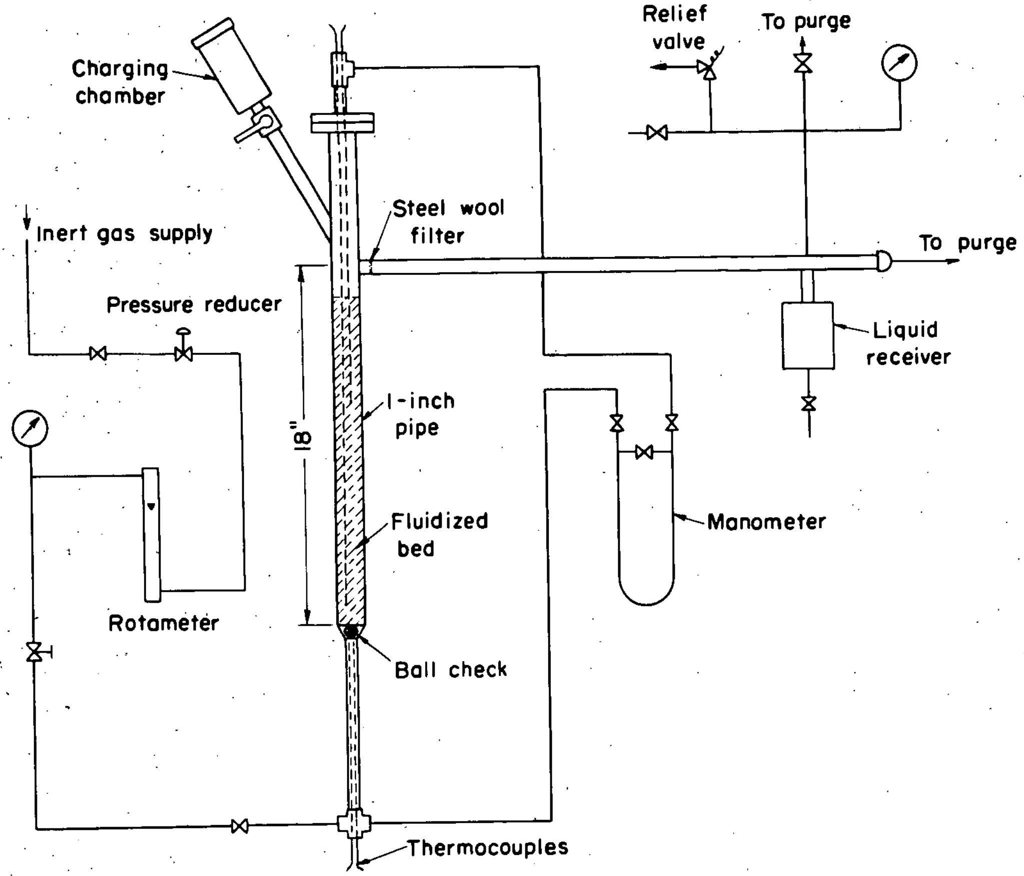

Fig. 6.-ONE-INCH REACTOR FOR CARBONIZATION TESTS